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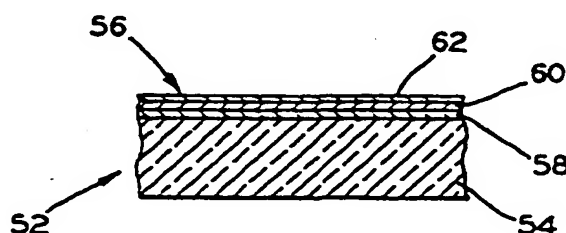
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(71) Applicant: LIBBEY-OWENS-FORD CO. [US/US]; 811 Madison Avenue, Toledo, OH 43697 (US).  
(72) Inventor: SOUBEYRAND, Michel, J.; 7935 North Shoreline Drive, Holland, OH 43528 (US).  
(74) Agent: OBERLIN, Phillip, S.; Marshall & Melhorn, 8th floor, Four SeaGate, Toledo, OH 43604 (US).

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(54) Title: GLASS COATING METHOD AND GLASS COATED THEREBY

(57) Abstract

A glass substrate (54) is coated by CVD with a multilayered coating (56) comprising a base, intermediate and top layers (58, 60 and 62), respectively, wherein the layers are silica, metal oxide, metal nitride, metal carbide and silica complex, etc. In the CVD of silica-containing coating on the glass substrate, silane, oxygen, a radical scavenger gas such as ethylene and a carrier gas are combined as a precursor mixture.



**TITLE****GLASS COATING METHOD AND GLASS COATED THEREBY****BACKGROUND OF THE INVENTION**5     **1. Field of the Invention**

The present invention pertains to a process for applying a coating to glass, and more particularly to a continuous chemical vapor deposition process, commonly known as a CVD process, for application of a silica coating to a glass substrate.

10     **2. Description of the Prior Art**

Silica coatings are commonly applied to glass substrates alone or in combination with various other coatings for modifying characteristics of the glass for use in vehicles and for architectural purposes. Typically, such coated glass is produced by continuously coating a glass substrate during its manufacture by a process known as the float glass process. In accordance with this process, molten glass is deposited on an enclosed elongated bath of molten tin over which a non-oxidizing atmosphere is maintained to prevent oxidation of the tin. The molten glass is allowed to spread under controlled conditions to establish a ribbon of predetermined width and thickness, and the ribbon is gradually cooled as it is pulled across the bath for removal as a continuous ribbon upon lift out rolls at the exit end of the bath. Thereafter the continuous ribbon is conveyed through an adjacent enclosed annealinglehr upon a series of aligned rolls for gradual cooling in accordance with a

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coatings in the float bath has suggested as precursor gases a mixture consisting of silane ( $\text{SiH}_4$ ), constituting the source of silicon, and an electron donor compound such as an ethylenic compound. As the sole source of oxygen capable of associating with the silicon atoms arising from the decomposition of the silane, this process relies upon a certain proportion of the oxygen atoms of the glass substrate diffusing to the surface. The diffusing may be enhanced by adsorption of the electron donor at the surface of the glass. The capacity for diffusing, however, is very limited and the resulting films are not of adequate thickness for many purposes.

U.S. Patent No. 5,304,394 discloses a process using only a silane and an ethylene compound for obtaining a coating based upon silicon, oxygen and carbon and having a satisfactory thickness without utilizing a supplementary oxygen source. More particularly, it is suggested that by increasing the contact time between the precursor gases and the glass it is possible to amplify the diffusion of oxygen through the thickness of the glass, and by providing sufficient minimum proportions of silane and ethylene, to utilize this oxygen in forming a coating having the desired increased thickness. The necessary contact time is achieved through appropriate selection of the length of the deposition zone and the speed of the glass substrate as it moves through the zone. Due to the requirement for achieving the necessary contact time, such a procedure may not be readily

Laboratory tests conducted with precursor lines and coater surfaces maintained at 250°F, and on-line tests with components similarly at 200°F, indicate premature burning does not occur. The presence of the radical scavenger presents a further  
5 advantage in that it contributes to the control of and permits optimization of the kinetics of the chemical vapor deposition (CVD) reaction on the glass. While the preferred combination of precursor materials includes monosilane ( $\text{SiH}_4$ ), ethylene ( $\text{C}_2\text{H}_4$ ) and oxygen, with ethylene functioning as the radical scavenger,  
10 it is contemplated that other and different materials may be employed in the combination as the radical scavenger.

#### BRIEF DESCRIPTION OF THE DRAWING

In the drawings, wherein like numerals refer to like parts  
15 throughout:

Figure 1 is a schematic, longitudinal, vertical sectional view of an apparatus for practicing the float glass process and including gas distributor beams positioned for applying coating material in accordance with the invention;

20 Figure 2 is a fragmentary sectional view of a coated glass article produced in accordance with the invention; and

Figure 3 is an enlarged schematic end view of a gas distributor beam suitable for use in practicing the invention.

A suitable non-oxidizing atmosphere, generally nitrogen or a mixture of nitrogen and hydrogen in which nitrogen predominates, is maintained in the bath enclosure 34 to prevent oxidation of the tin bath. The atmosphere gas is admitted through conduits 44 operably coupled to a distribution manifold 46. The non-oxidizing gas is introduced at a rate sufficient to compensate for normal losses and maintain a slight positive pressure, on the order of about 0.001 to about 0.01 atmosphere above ambient atmospheric pressure, so as to prevent infiltration of outside atmosphere. Heat for maintaining the desired temperature regimen in the tin bath 26 and the enclosure 34 is provided by radiant heaters 48 within the enclosure. The atmosphere within thelehr 20 is typically atmospheric air, while the cooling section 22 is not enclosed and the glass ribbon is open to the ambient atmosphere. Ambient air may be directed against the glass ribbon as by fans 50 in the cooling section. Heaters (not shown) may also be provided within the annealing lehr for causing the temperature of the glass ribbon to be gradually reduced in accordance with a predetermined regimen as it is conveyed therethrough.

As heretofore indicated a glass article in accordance with the invention may include a coating comprising a single layer of a silica complex, or there may be provided a multilayered coating wherein the silica complex comprises any one or more of the layers. There is illustrated in Fig. 2 a glass article embodying the present invention, indicated generally at 52 and

A conventional configuration for the distributor beams 64, 66 and 68 suitable for supplying the precursor materials in accordance with the invention is shown more or less schematically in Fig. 3. A framework 70 formed by spaced inner and outer walls 72 and 74, defines enclosed cavities 76 and 78 through which a suitable heat exchange medium is circulated for maintaining the distributor beam at a desired temperature. Precursor materials supplied through a fluid cooled supply conduit 80 extending along the distributor beam are admitted through drop lines 82 spaced along the supply conduit to a delivery chamber 84 within a header 86 carried by the framework 70. Precursor gases admitted through the drop lines 82 are discharged from the delivery chamber 84 through a passageway 88 toward and along the surface of the glass in the direction of the arrows in Fig. 3. Baffle plates 90 may be provided within the delivery chamber for equalizing the flow of precursor materials across the distributor beam to assure that the materials are discharged against the glass in a smooth, laminar, uniform flow entirely across the beam. Spent precursor materials, as well as a certain amount of the surrounding atmosphere around the beams, are collected and removed through exhaust chambers 92 along the sides of the distributor beam. Various types of suitable distributor devices for chemical vapor deposition are generally known in the prior art as disclosed, for example, in U.S. Patents Nos. 4,504,526 and 5,065,696.

It has been found that by combining a suitable radical scavenger compound and oxygen in selectively controlled amounts with the silane-containing gas, not only can ignition of the precursor materials be prevented, but also the kinetics of the silica deposition reaction can be optimized. Examples of suitable radical scavenger compounds are selected hydrocarbons, and particularly propylene and ethylene. By using the radical scavenger in combination with silane and molecular oxygen, ignition of the potentially explosive mixture at the temperatures required for reaction can be prevented, and the rate of reaction can be controlled to spread the reaction over the entire coating area beneath the gas distributor beam. As a result, both the deposition rate and coating uniformity can be maximized. Silane conversion efficiency is also greatly increased, so that chemical consumption and powder generation are minimized, resulting in much longer run times between shutdowns for equipment cleaning.

Heretofore, in forming silica coatings for color suppression in coating structures on glass, it has been customary to employ, among others, a dichlorosilane/oxygen system or a silane/ethylene/acetone system. In order to achieve the low haze and low emissivity which is a prerequisite for the color suppression structure in coated glasses now under development, it is highly desirable to use chlorine-free precursors. The silane/radical scavenger/oxygen precursor of the present invention not only represents such a chlorine-free

The trials involved a three layer stack configuration as illustrated in Fig. 2, with the base and top layers 58 and 62 being conventionally-produced tin oxide layers. The three layer stack configuration was employed in order to facilitate measurement of the thickness of the silica coating 60, since measurement of silica alone on glass is time-consuming and lacks accuracy when the coating thickness is less than 500 Angstroms. The glass temperature in front of the gas distributor beam 64, by which the base layer 58 is deposited, was about 1290°F (699°C).

Ethylene ( $C_2H_4$ ) was employed as the radical scavenger gas, with monosilane ( $SiH_4$ ) as the silicon-containing gas. It is contemplated that other hydrocarbons, particularly olefins, may serve as the radical scavenger compound so long as they inhibit premature ignition of the precursor materials, serve to control the kinetics of the CVD reaction on the glass, and do not produce byproducts which are detrimental to the float glass environment or structure. Ethylene has been found particularly well-suited in this regard. Although other gases containing silane may suitably be employed so long as they react to form the desired silica coating and no undesirable side effects are produced, monosilane is the presently preferred precursor material since it is readily available at reasonable cost.

Pure oxygen may be utilized as the precursor component. However, the components of atmospheric air are generally compatible with the environment of the distributor beam and the



In a first series of tests, eighteen computer-designed experiments were run. The process variables and corresponding levels were derived from previous laboratory experimentation, and were chosen to cover the range of deposition rates required at a line speed of 550 inches (13.97 meters) per minute to produce a 250 Angstrom silica layer (which is suitable for color suppression). Process variables were run at the following levels:

10	Flow Rate	116 - 138 - 159
	(Standard liters per minute per meter of beam length)	
	Silane Concentration	0.8% - 0.9% - 1.0%
15	Ethylene/Silane Ratio	3 - 6 - 9
	Oxygen Concentration	3% - 5% - 7%

For each set of test parameters, two transverse strips were cut from the glass ribbon at 5 minute intervals, and on each strip the properties were measured at three locations, left side, center and right side. Silica thickness, top tin oxide thickness, emissivity and haze were measured. The properties were determined at the three locations for each strip, and the properties reported are the averages of the six measurements. In addition, the strips were visually inspected for uniformity and appearance rated according to the following schedule:

	Poor:	0	Fair+:	3
	Fair-:	1	Good-:	4
30	Fair:	2	Good:	5

TABLE I (CONTINUED)

Experi- ment No.	Emissivity	Haze	Top Tin Oxide Layer Thickness (Å)	Visual Appearance
1	0.20	0.40	2294	0
2	0.19	0.40	2352	1
3	0.18	0.40	2416	5
4	0.19	0.40	2386	2
5	0.19	0.43	2387	5
6	0.19	0.43	2360	5
7	0.21	0.38	2235	3
8	0.24	0.35	2237	0
9	0.25	0.40	2205	0
10	0.19	0.47	2362	5
11	0.27	0.40	2211	0
12	0.20	0.43	2315	4
13	0.21	0.42	2269	3
14	0.20	0.43	2322	5
15	0.24	0.43	2237	0
16	0.21	0.42	2296	1
17	0.28	0.42	2236	0
18	0.22	0.40	2268	3

TABLE II

Experi- ment No.	Silane Concen- tration (%)	Flow Rate (SLPM/per meter of length)	Ethylene /Silane Ratio	Oxygen Concen- tration (%)	SiO <sub>2</sub> Thick- ness (Å)
19	0.70	138	9.0	4	187
20	0.80	138	9.0	4	240
21	0.60	159	9.0	2	204
22	0.80	159	12.0	6	291
23	0.80	159	12.0	2	274
24	0.80	116	12.0	2	239
25	0.80	116	12.0	6	222
26	0.70	116	9.0	6	163
27	0.60	116	12.0	4	158
28	0.70	138	12.0	2	226
29	0.60	138	6.0	6	165
30	0.60	159	12.0	6	167
31	0.80	159	6.0	6	257
32	0.80	159	6.0	2	291
33	0.70	159	6.0	4	218
34	0.80	116	6.0	2	249
35	0.80	116	6.0	6	212
36	0.70	138	9.0	4	202
37	0.90	138	9.0	3	282
38	0.65	159	5.8	2	220
39	0.69	159	5.5	2	243
40	0.80	116	16.6	2	229

It has been determined that an optimum thickness is achieved when the ethylene/silane ratio is equal to about 9 to 1. At lower ethylene levels the reaction is rapid so as to occur directly beneath the passageway 88 through which the precursor gases are discharged. Although the reaction occurs rapidly, a small portion of the coating area is utilized and maximum thickness of the silica layer is not achieved. At higher ethylene levels the reaction is slower, and thus extends toward the exhaust chambers 92 so that some of the precursor materials may be exhausted before reacting. The coating area is thus insufficiently utilized and the silica deposition rate drops. At intermediate levels of ethylene, reaction occurs over the entire coating area beneath the gas distribution beam so as to maximize the deposition rate and thus the thickness of the silica layer. For example, utilizing a precursor comprising 1.8% silane, 16.2% ethylene and 5.4% oxygen has been found to produce a silica-containing coating of about 600 Å at a line speed of 466 inches (11.8 meters) per minute.

The results of the experimental series also show that ethylene is necessary to achieve acceptable coating uniformity. At low ethylene levels, the silane/oxygen mixture is excessively reactive on the hot substrate, resulting in flow disturbances and coatings defects such streaks, blotches, etc. Ethylene not only prevents ignition of the precursor mixture, but also plays an important role in controlling the kinetics of the deposition reaction in the coating zone. This, in turn, contributes to

## WHAT IS CLAIMED IS:

1. A process for depositing a silica-containing coating upon a glass substrate comprising the steps of:

5 a) providing a glass substrate at an elevated temperature having a surface upon which the coating is to be deposited;

10 b) directing a precursor mixture including a silane, a radical scavenger gas, oxygen and an inert carrier gas, toward and along the surface to be coated and reaching the mixture at or near the surface to form the silicon-containing coating, the radical scavenger being present in an amount adequate to prevent ignition of the precursor gases and to regulate the rate of reaction of the mixture; and

15 c) cooling the coated glass substrate to ambient temperature.

2. A process for depositing a silica-containing coating upon a glass substrate as claimed in claim 1, including:

20 d) before step b) depositing onto the surface a coating of silicon, metallic oxide or metallic nitride.

3. A process for depositing a silica-containing coating upon a glass substrate as claimed in claim 1, including:

25 d) after step b) depositing onto the surface a coating of silicon, metallic oxide or metallic nitride.

9. A process for depositing a silica-containing coating as claimed in claim 1, wherein the silane is monosilane ( $\text{SiH}_4$ ) and the radical scavenger is ethylene ( $\text{C}_2\text{H}_4$ ).

5 10. A process for depositing a silica-containing coating as claimed in claim 9, wherein the silane concentration in the precursor mixture is between about 0.05% and 3.0% by volume.

10 11. A process for depositing a silica-containing coating as claimed in claim 9, wherein the ethylene/silane ratio is between about 3 to 1 and 17 to 1.

15 12. A process for depositing a silica-containing coating as claimed in claim 9, wherein the oxygen concentration in the precursor mixture is between about 0.15% and 9% by volume.

20 13. A process for depositing a silica-containing coating as claimed in claim 10, wherein the ethylene/silane ratio is between about 3 to 1 and 17 to 1 and the oxygen concentration is between about 0.15% and 9% by volume.

25 14. A process for depositing a silica-containing coating as claimed in claim 13, in which the ethylene/silane ratio is about 9 to 1.

17. A method of producing a glass sheet substrate having a silica-containing coating on one surface thereof as claimed in claim 15, including the step after b) of depositing onto said one surface a coating selected from the group consisting of silicon, metallic oxides and metallic nitrides.

18. A method of producing a glass sheet substrate having a silica-containing coating on one surface thereof as claimed in claim 15, wherein said non-oxidizing atmosphere comprises a mixture of nitrogen and hydrogen in which nitrogen predominates, said silane comprises monosilane, said radical scavenger gas comprises ethylene, and said inert carrier gas comprises nitrogen.

19. A method of producing a glass sheet substrate having a silica-containing coating on one surface thereof as claimed in claim 18, wherein the monosilane concentration is between about 0.05% and 3.0% of the precursor gas by volume, the oxygen concentration is between about 0.15% and 9% by volume of the precursor gas, and the ethylene/silane ratio is between about 3 to 1 and 17 to 1.

23. A glass substrate having a silica-containing coating thereon as claimed in claim 22, wherein said plurality of coating layers includes at least one layer selected from the group consisting of silicon, metallic oxides and metallic nitrides.

24. A glass substrate having a silica-containing coating thereon as claimed in claim 22, wherein said silica-containing coating comprises any one of said plurality of coating layers.

25. A glass substrate having a silica-containing coating thereon as claimed in claim 23, including at least two of said silicon-containing coatings separated by at least one coating of silicon, metallic oxide or metallic nitride.

26. A glass substrate having a silica-containing coating thereon as claimed in claim 21, wherein said elevated temperature is at least about 600°F (316°C).

27. A glass substrate having a silica-containing coating thereon as claimed in claim 22, wherein said elevated temperature is at least 1050°F (566°C).



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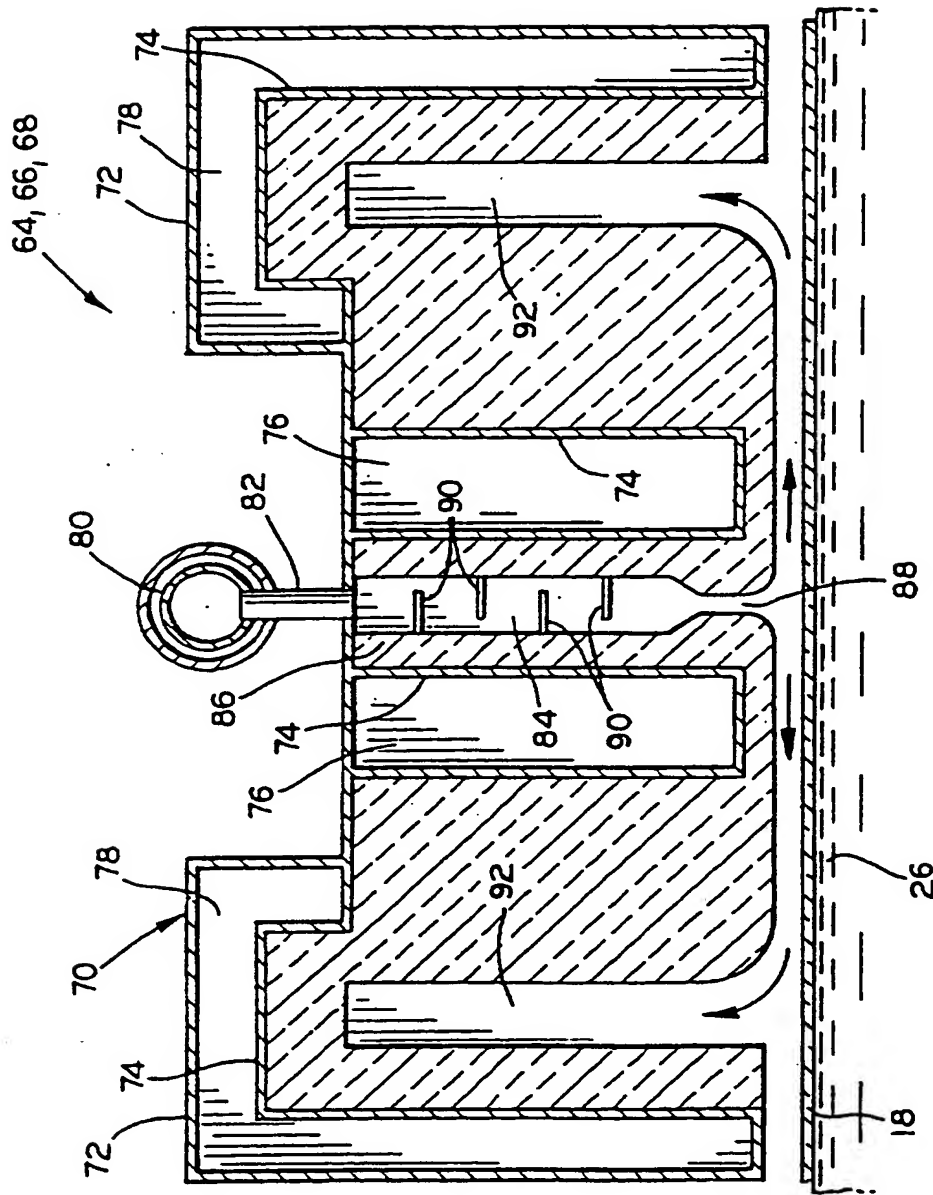


FIG. 3